

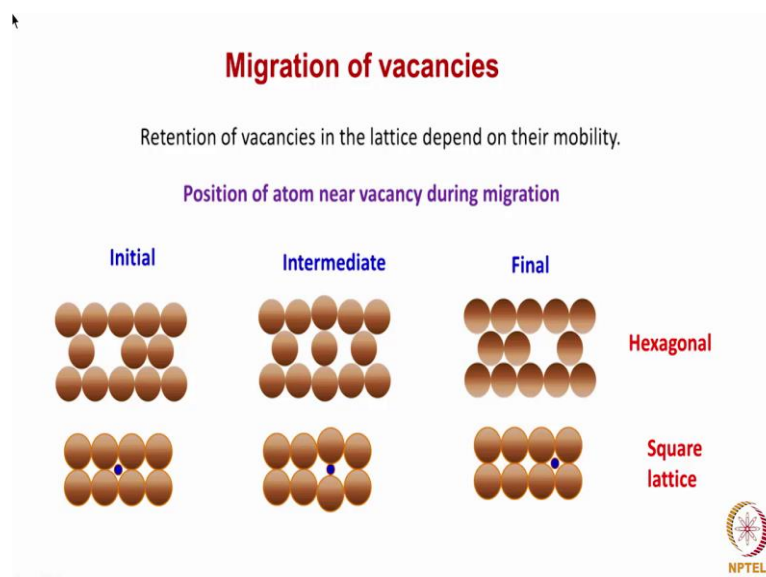
**Defects in Materials**  
**Prof. M Sundararaman**  
**Department of Metallurgical and Materials Engineering**  
**Indian Institute of Technology, Madras**

**Lecture – 09**  
**Vacancy Concentration Determination-1**

In the last class, we talked about or discussed about the various types of point defects their configuration which here just in geometrical configuration how they look like. And then about we also discussed about the equilibrium concentration of vacancies which we can form in a material.

But now what is important is that once vacancies have been generated in the material these vacancies will be it is they are not going to remain static at high temperatures they will be moving around. The migration energy is going to decide what is going to be the net concentration of vacancies which should be present in a material. Suppose some excess concentrations of vacancies are going to be there, what is the rate at which the concentration will reach the equilibrium concentration will be the decided by how fast or how slow they migrate. Let us look about the migration energy of vacancies.

(Refer Slide Time: 01:22)



When we talk of the migration energy of vacancies first thing we you have to look at it if a vacancy has to move from one position to another position, what is the mechanism by which this happens? These which we are considered a hexagonal 2 dimensional lattice in

which a vacancy is created in this particular position that is if an atom moves from here to this particular position then the vacancy might have shifted from this position to this position, correct, for that to happen, the first thing which should happen is that this atom should come and reach a position; that means, that the gap is not sufficient for this atom in this hard shear model to jump to the next site.

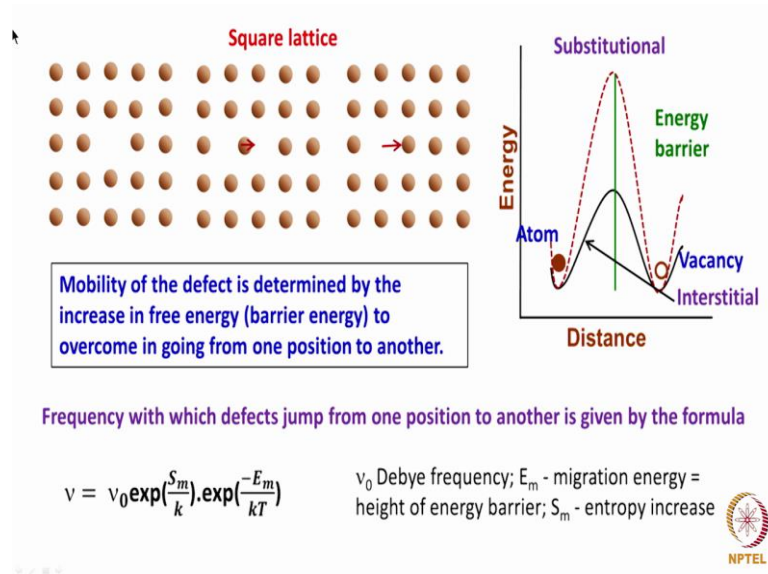
That means that some energy is required or it has to strain that push the atoms on that adjacent atoms and then come jump to that site what are the ways in which it can happen in the material in a real material all the atoms are vibrating around their lattice positions and the vibration increases depending upon the temperature at which the material either with respect to its melting point in such a case what is going to happen is that during this vibration it so happens that the atom at that top this particular atom moves in this direction these atom moves in this direction and the thermal vibration is decides what is the way in which will be moving.

So, it can so happen that some with less energy it can just move from this reach this position into (Refer Time: 03:06) position when this has reached this intermediate position from this intermediate position how is it going to come to this pattern? There are 2 possibilities, it is just a probability either it can jump back to this position or it can jump into the side if it jumps into the left side then the defectors moved. That is what essentially has to happen the same thing will happen we are taking a square lattice where an interstitial atom is put in this position correct.

Student: (Refer Time: 03:39).

This interstitial atom if it has to just jump to this site first it has to come into this middle position where it is occupying which is at a strain state from which you can either jump to this side or this side if it makes a jump to the right side then we feel they see that the interstitial atom as moved. So, essentially what we can understand looking at this diagram is that it all depends upon the vibrational frequency there are many atoms are being made when it is vibrating it, but chance that it will succeed is not the same as a vibrational frequency correct.

(Refer Slide Time: 04:24)



Now, let us look at the same case which I am showing it in a square lattice where it is not a hard sphere model. So, an atom has to from this atom vacancies that it has to come to this position and from this position it has to jump then only the vacancy will shift from here to here correct I think this arrow should have been pointed in the other direction the same thing can be explained in an another way we can look at the energy diagram that is energy diagram is that if an atom moves from this particular position to if it comes to an adjacent position, what is it which is going to happen the same energy will be there that just going to be at the saddle point, but to reach that position, it has to overcome some energy barrier if it is going to be a substitutional atom.

The energy barrier could be very high are for an interstitial atom the energy barrier could be small 2 things which are happening one is a thermal vibration which is giving some energy to the atom and that makes atoms vibrate and it can increase or decrease the gap that is one and then another is atom sitting on the adjacent one is trying to jump from here into this site because that also is all the 3 direction of 4 6 directions, it can equally vibrate with the same frequency then when that happened some of the jumps are successful.

Now, this we can try to find out with respect to what is the probability if this is the energy which is required the; what is the strain energy which is required which has to be overcome. So, that the atom can move from easily from one to the other to the energy

which is available it can be returned in terms of probability and on that basis if you try to look at it this is the sort of an expression which we will be getting it where  $\nu_0$  is the debye frequency  $\nu_0$  is the debye frequency then there is an exponential term which depends upon the migration entropy and this is the one which is  $E_m$  is going to be the migration energy which is required.

This migration energy will consist of one the strain energy part of it and another energy also which will come in that picture not only the strain energy it is what is going to be the bond energy between these atoms also will come into the picture both of them will decided the  $E_m$  generally it has been seen that this terms turns out to be close to one in the FCC materials. So, it can be written like  $\nu_0$  into this factor. So,  $\nu_0$  is the debye frequency with which the maximum frequency with which an atom vibrates around the lattice sites and this in this specific case this is considered as the height of the energy barrier.

(Refer Slide Time: 08:06)

**Jump frequency of vacancy for different  $E_m$  at different temperatures**

$E_m$ (eV)	$\nu$ at 77K	$\nu$ at 300K	$\nu$ at 773 K	$\nu$ at 1273 K
0.1	$2.9 \times 10^6$	$2.1 \times 10^{11}$	$2.2 \times 10^{12}$	$4.0 \times 10^{12}$
0.5	$\ll 1$	$4.0 \times 10^4$	$5.5 \times 10^9$	$1.0 \times 10^{11}$
1.0	$\ll 1$	$\ll 1$	$3.0 \times 10^6$	$1.1 \times 10^9$
2.0	$\ll 1$	$\ll 1$	1	$1.2 \times 10^5$

*Kelly and Knowles book on Crystallography and crystal defects*

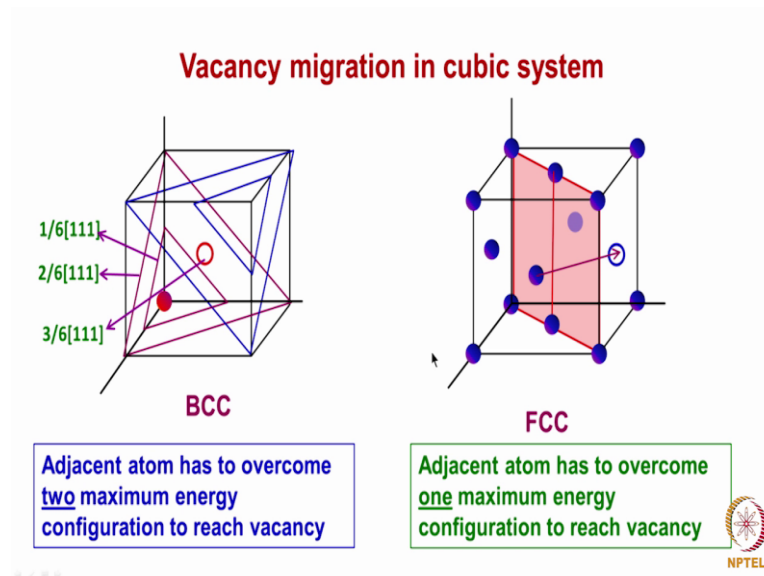


So, this in the literature where the calculations have been done for the various migration energy from our 0.1 to 2 electron volt and then we look at the different temperatures what is the rate at which the success rate at which the atom will jump from one site to another site or vacancy will jump from one vacant site to another vacant site. So, this if you look at it; it turns out to be less than one frequency for 2 electron volt whereas, 0.1 is electron volt is a migration energy is 2.9 and the same thing if you can see for a 2

electron volt migration energy what it requires is 1.2 into 10 to the power of 5 jumps, it will be making it this table just shows that what is the sort of successful jumps which will take this is also going to decide how fast the defect is going to move.

So, the rate at which the defects moves at any particular temperature depends upon the migration energy term in the case of vacancy generally this energy term is also the same as that of what the energy of formation of the vacancy especially for the case of copper and all these material.

(Refer Slide Time: 09:38)



So, it turns out to be rather very high about one electron volt or more; that means, that the rate at which the vacancies move is slow, we will talk about it interstitial when we come to that.

Then the next question comes also is that in different lattices if we consider suppose there is an atomic site an atomic cubic lattice BCC lattice, if we consider this is an atom fail at the middle of it I had shown an open circle what it means is that there is a missing atom is there. If an atom has to jump from here to reach this position in between if we look at it the layers which are shown with the brown colour that with the brown lines the triangles which are shown that shows the different layers. So, if this is a layer there are 2 more layers which it has to overcome to reach here. So, when it jumps from here to here it is not one barrier which it has to overcome 2 barriers are going to be there, there is an atom has to be squeezed in that that is what essentially is being shown here there is a

layer at 1 by 6 111 position a layer at 2 by 6 111 position and 3 basics 111 position is where this vacancy is there.

That means that if an atom jumps from here these layers have to be squeezed when they are vibrating a part it will jump from there to an in between position then it. So, happens that the other layers also the atom positions they would expanded moved away in such a case that atom will jump from this position to this position. So, in between there is a point which requires energy let us compare to that of the other 2 layer these what it happens in the case of a BCC lattices, this we can find out for various lattices how what will be the weather is a one saddle point which is going to be there in the energy are made more than one there are weather intermediate stages where it can remain also where energy is less, in the case of FCC.


If we consider it here it moves from this particular position to an adjacent vacant site it is only the atom on the in between layers that is only one layer which the migration energy if it is able to overcome that migration energy then it will be coming into that vacant position it will jump.

(Refer Slide Time: 12:18)

**Distortion around vacancy**

Crystal		Shell	
Metal	Structure	First	Second
Pb	c.c.p.	1.42	-0.43
Ni	c.c.p.	2.14	-0.39
Cu	c.c.p.	2.24	-0.40
Ca	c.c.p.	2.73	-0.41
Fe	b.c.c.	6.07	-2.12
Ba	b.c.c.	7.85	-2.70
Na	b.c.c.	10.80	-3.14

**Relaxation larger in bcc than in fcc**

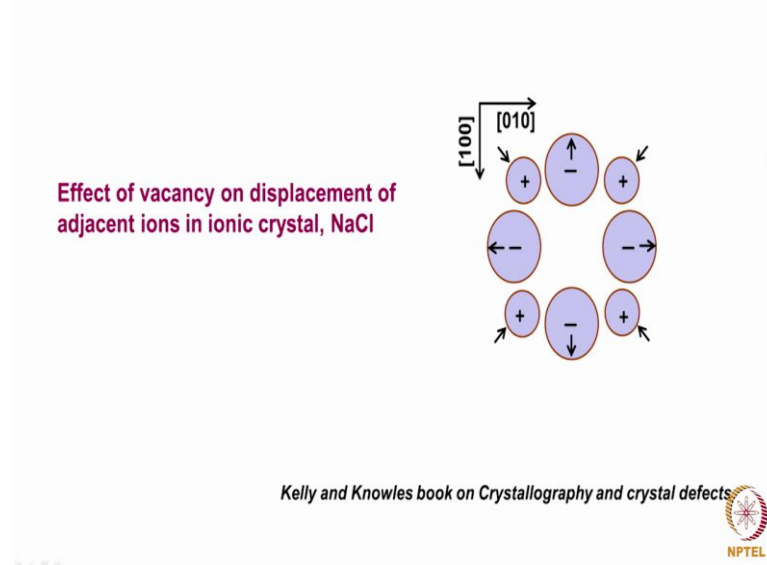
*Kelly and Knowles book on Crystallography and crystal defects* 

So, from this simple example you can see that what is that even in different materials depending upon the crystal structure the type of free energy barrier which has to overcome the shape of the free energy barrier is going to be different in this particular view graph what I am just trying to show is that for various types of crystal structure

BCC and FCC if a vacancy is created how the atoms are going to be adjacent atoms what is the displacement which takes place to the adjacent atom here.

If we look at it this first shell is what it means positive means that the atoms move closer towards the vacant site the negative means that the atoms are moving away from the vacant site here if we look at it in the case of FCC the relaxation is less whereas, in this case the moment is going to be quite large in the case of BCC which is an open structure.

(Refer Slide Time: 13:32)

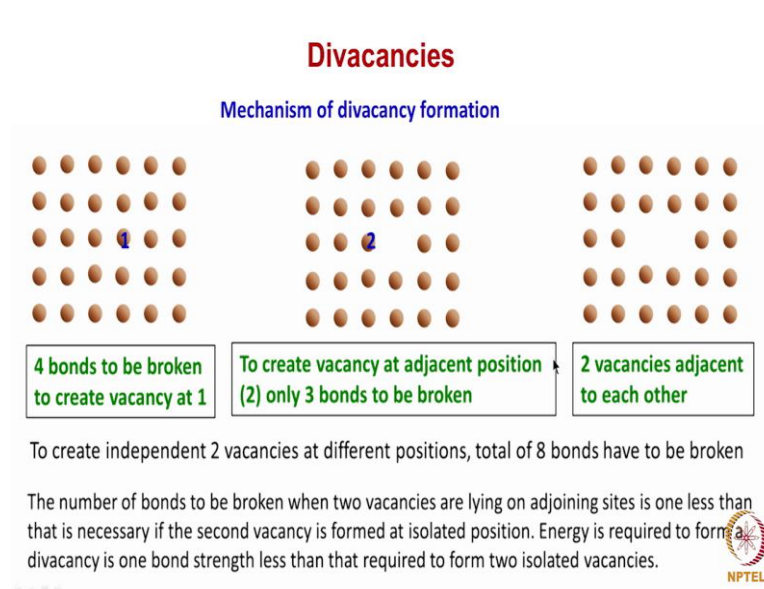


The same thing if you look in the case of a ionic material they are in addition to this moment of atoms there are relaxation taking place this is controlled by the net charge balance also correct suppose if we look at this case of a sodium chlorate the positive ion there is a vacancy in this anion site when there is a vacancy in the anion site we can see the anion state; that means, that the positive not a cation site when the cation has been removed from here. Now what is going to happen is that this is the one which was attracting the anion steed.

Now, since that is neither they will be repelling away it is different from what we have seen it in the case of metallic material then and anions catian what will happen is that since one cation has gone from here they will be moving in exactly opposite to what we have seen it in the case of a metallic system which will happen effectively. There are going to be relaxation and this relaxation is determined by the electronic configuration

they are own that defect decides how the irons displaced from their equilibrium lattice site.

(Refer Slide Time: 15:00)



Then so far what we considered is that only one vacancy is being produce is it that only one vacancy a single vacancy is produced always are suppose these vacancies are moving that is a chance which can happen that 2 vacancies come close to each other adjacent site then what will happen in such a case if they join together they can create where 2 sites are vacant this sort of configuration is called as a deviancy what I am considering it is a case where this particular atom which is positioned marked as one a vacancy is created then vacancy is created in that to create a vacancy in that site in these 2 dimensional lattice 4 bonds have to be broken to create a vacancy. So, then this is how it will look like correct 4 bonds are broken that atom has been removed and I have not shown that position it may be sitting on the surface somewhere.

Suppose at this position I am trying to remove an atom from this site and create a vacancy here again we have to break 4 bonds correct suppose an atom from these particular position 2, I create a vacancy then how many bonds have to be broken only 3 bonds; that means, that an adjacent item you should try to remove and try to create a vacancy there is it is easy. That means there is a reduction in energy is going to be there. So, compared to 2 vacancies if already vacancy exists it is always likely that a removal an atom from an adjacent site one can create a divacancy and compared to 2 vacancies



moving separately if a divacancy is created, there is a reduction in energy because one bondless is to be broken. This suggests that always there is a possibility method divacancies could be produced in this material correct.

So, this is what essentially I am giving it here, now this is the final configuration, there will be a 2 adjacent vacancies are there. So, if independent vacancies we are creating it to vacancies eight bonds to be broken if it is an adjacent sites we require only in a 2 dimensional lattice 4 bonds only as to be not 4 it is essentially seven bonds to be broken in this case to create a divacancy.

(Refer Slide Time: 18:11)


**Divacancies**

Equilibrium concentration of divacancies,  $n_d$  is given by the formula

$$N_d \propto \exp\left(-\frac{(2E_f - E_b)}{kT}\right) \qquad \frac{n_d^2}{n_e N} = q \exp\left(-\frac{E_b}{kT}\right)$$

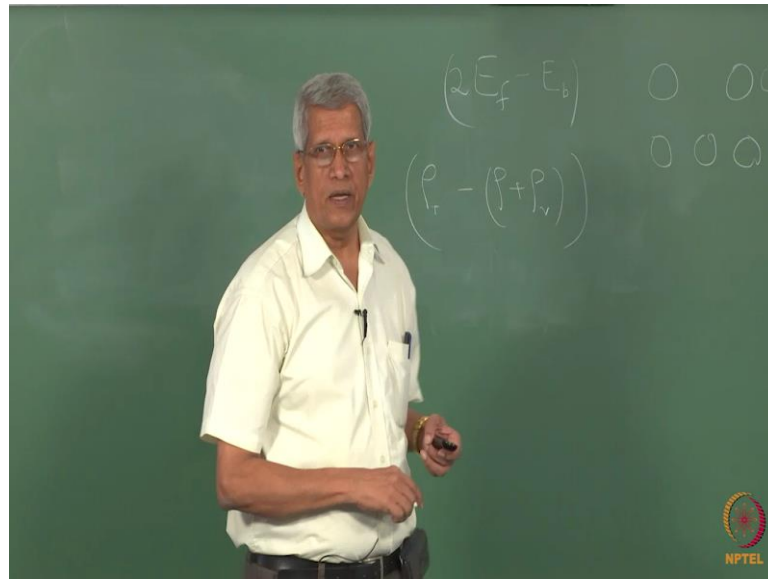
$q$  depends on the entropy of formation of defects and divacancies

The ratio of divacancy to single vacancy is given by the ratio

$$\frac{n_d}{n_e} = (1/q) \exp\left(\frac{S_T}{k}\right) \exp\left(-\frac{(E_f - E_b)}{kT}\right)$$


So, using this information one can calculate what will be the concentration of vacancies which are going to be there. So, what will be the formation energy of the divacancy 2 vacancies to form independently, what is the formation energy minus?

(Refer Slide Time: 18:39)



So, if 2 vacancies is to be form this is going to be the formation energy twice minus  $E_b$  is the energy for one bond to be broken. So, this is what is going to be the net free energy which is required energy which is going to formation of a divacancy.

Similar to a vacancy for which single vacancy we have looked at the concentration of the defect we can look at it in this case also. So, the number of vacancy concentration will be proportional to exponential minus twice  $E_f$  minus  $E_b$  by  $kT$ , correct and then we know for a single vacancy, what is going to be the value? Similar formula is there substituting for  $E_f$  by  $kT$  that terms and doing some algebra will be able to get some ratio of the divacancies to the single vacancies these are given by this formula which depends only on in this specific case a way form in which it is returned under binding energy that is that energy which is required for breaking of 4 bond to each one term depends upon the entropy of formation of the definitional divacancy this ratio if you try to write it this will finally, turn out to be that  $n_d$  to  $n_E$  that is a single vacancy equilibrium concentration of vacancy to a divacancy this will turn out to be depends upon the energy of formation of a vacancy minus the one which is the energy which is required for a single bond to be broken are the bond energy.

Generally, what has been seen is that this ratio turns out to be less than 10 less than 20 percentage close to melting point where the defect concentration of a single vacancies itself we consider to be about  $10$  to the power of minus 4 suppose 3 vacancies join

together then what will happen still there can be a reduction in energy could be there, but at the same time when you look at this that energy term becomes very large correct.

Student: Yes.

Overall energy terms become large because of that the formation energy of a divacancies are such high compared to that of a single vacancy. So, the number of divacancies which will be produced will be less similarly that try vacancies will be less, but still there is a probability, but that probability increases as we raise the temperature correct what is going to be a consequence whenever we look at the diffusion equation we say that this is the rate at which an atom diffusers.

And try to find out how the particular phase transformation is going to take place on that basis. When these defects are present their moment is much faster, because of which the rate at which the growth rate takes place of (Refer Time: 21:57) that could change a lot. So, it is not only that the; at the single vacancies both divacancies, trivacancies all these things also do participate and control the kinetics of the reaction a kinetics of the reaction can change. So, if you have to understand that we should know about a concentration of this defects are also which are being present in the material.

Now, I will talk about so far we talked about only vacancies, interstitials just a configuration we have looked at it what all the types of interstitial (Refer Time: 22:36) what are the equilibrium concentration these interstitials can have that is what we wanted to discuss what are the type of interstitial which can have self interstitial and the impurity atoms also could occupy interstitial positions as I mentioned earlier.

(Refer Slide Time: 22:56)

**Interstitial Defects**

Self Interstitials  
Impurity atoms as interstitials


How are self interstitials produced ?

Frenkel defects - Self ion irradiation

Dislocation - dislocation interaction / non conservative motion of dislocations

When vacancy is created atom is shifted to equivalent position in crystal.

When interstitial is created, atom occupies a non equivalent position in the lattice. Different configurations possible and one with the lowest energy has to be identified

  
NPTEL

Then what are the other in information which we require is that how are these intersections produce the way in which this interstitials are produced is one they can be produced as a freckle defect during ion irradiation or during deformation also these interstitials could be produced, because especially when creep process takes place either it is a prime up or down depends upon whether a vacancy is emitted are an interstitial is emitted. From that site these all are the other ways in which these sort of defects could be producing in the lattice.

And another thing also which we mentioned is that when vacancy is created. It is essentially removing an atom from a specific lattice site, but when we put an interstitial it can occupy any particular position. And not only that, that from there it can jump to many equally not only equivalent non-equivalent positions are also available in the lattice to which the interstitial can jump the probability of that occurring is some finite value is there though it may be negligibly small in some cases.

(Refer Slide Time: 24:10)


**Structure of self interstitials in fcc**

● Metal atoms  
○ Octahedral interstices  
○ Tetrahedral interstices

C.Hammond, Basics of crystallography and diffraction

**Formation energy ~ 3-4 eV ; Migration energy ~ 0.1 to 0.3 eV Cu**

When interstitial is created, atom occupies a non equivalent position in the lattice.  
Different configurations possible.  
One with the lowest energy is stable



So, here is what we are considering, it is just what does the way in which interstitial; what is the position then a if you put a self interstitial atom are an impurity which has the same size all are smaller size, if it has to occupy what position, it can occupy in the FCC lattice there are industries which are available or octahedral industry sites are there these are especially if you look at the gap in then the center of the lattice our tetrahedral sites are there which correspond to if each of these cube is divided into eight smaller cubes.

The center of each of that cube will be the tetrahedral sites there also an atom can occupy the interstitial atom can come into that position be anyway. If we consider one of these faces here if you look at this 100 face. If we show these is what essentially we are showing the how the item positions atoms are going to occupy a position if an interstitial atom is introduced to in this the position which the industrial can occupy is being shown in this.

Now, what is going to happen in that this interstitial atom position if you look at it the adjacent atoms are very close by? So, the bond energy if you look at the repulsive force will be very high. So, these atoms will be rippled. So, the this is at a configuration which is energetically if you look at it is a very high energy configuration if by some over the other if the atoms can be moved a little bit relax.

So, that the distance between the atoms could be increased further then in that configuration that could be slight reduction in energy of this defect that is what

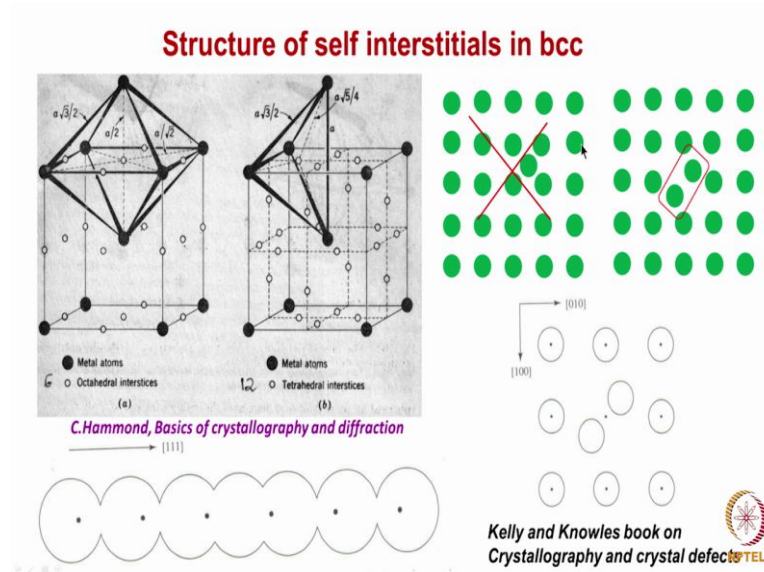
essentially is being shown in this. Next one here we can see that instead of it this atom is pushed a little bit here and this atom is also moves a little bit here now you can see that these 2 atoms are occupying positions where overall the separation between the atoms are increased this is the sort of configuration in which interstitial can exist and in the last 10-15 years people have done a lot of computer simulations on the material and they have seen that. In fact, this sort of configuration is energetically quite stable in the case of FCC material.

And another is also that when we put an interstitial to this position does it strain the lattice quite considerably. So, the energy which is required for formation of this interstitial is going to be very high because energy which was to push put to push the atom into that industrial site is very high. So, in copper, especially it has been seen that it is about 3 to 4 electron volt. Now since it is at a high energy configuration with a little bit of energy it can move from one position to another.

So, the migration energy which is required is at already that strain energy term is. So, high that is trying to push all the atoms farther away. So, it is to jump from one position to another position from this position to an adjacent position this is an un relax configuration the relaxed configuration will be pushed apart. So, it can easily jump onto it so; that means that the migration energy which is required is always less. So, interstitial requires less migration energy compared to vacancies and the case of (Refer Time: 28:16) from 0.1 to 0.3 electron volt. That means, that these defects can move really fast this is the reason why you see that in most of the materials interstitial defects when they are present like us when we do an irradiation vacancies and interstitials are produced vacancies move about slowly the self interstitials move very fast and they can come to surface.

So, seeing self interstitials is going to be more difficult and that is one of the reason why we always see the vacancy concentration is the only thing which we see in the material, most of the samples we do not see interstitial because interstitials when they are generated they move so fast. Is it clear?

(Refer Slide Time: 29:11)



And if we consider the type of defects which are going to be there in the BCC material; the BCC material, this is a position where octahedral sites which the interstitial atoms can occupy one is in this position another is in this position and I edge and this is on another position is an this edge then the various case you can occupy and this is at a tetrahedral position you assume that an atom is occupying a position like here I think it is better a in this specific position when it occupies that position here again the separation between the atoms if you see it, it turns out to be small if it pushes these atoms a little bit it can choose a configuration where the separation between the atom has increased considerably.

This sort of configuration is possible there is an another configuration which has been seen in many ordered dillies yes not order dillies in disorder dillies, but as during irradiation experiment is that if an atom comes into it there is a row of atoms that is essentially what it is going to be there if that if there are atoms are occupying at some specific separation if you introduce one atom here it is going to move the separation row players. These atomic positions are separation as reduce because one atom has been pushed into that position.


This sort of configuration is called as a (Refer Time: 31:08) this is one type of an interstitial configuration which has been seen in the material that is what you can make out that compared to vacancies now there are many types of configurations in which the

interstitials can exist in crystalline materials here what I have shown is that though this is the simple configuration which we considered initially, but what is the final configuration which actually has been seen in the real systems use of this type not what we earlier started about the different configuration.

(Refer Slide Time: 31:42)

**Experimental determination of point defects concentration**

- Vacancies**
  - Positron annihilation
  - Thermal expansion and XRD
  - Resistivity / Conductivity
  - Conductivity – for ionic crystals
- Interstitial impurities**
  - Internal friction



Now, let us look at suppose we wanted to find out the concentration of the defects both for interstitial as well as vacancy what are the information which you required in the case of vacancies what we require is that what is the concentration of the vacancy which is going to be there and its formation energy and the migration energy. If this information is available we will have complete information about how; what will; how much of that defect will be produced at each temperature and how they will and their kinetics both the information will be getting it there are many experiments which could be done to find out this concentration?

What is positron annihilation technique then another is thermal expansion and x ray diffraction could be used to find out that information resistivity is another technique which we could use it resistivity or conductivity both? It is the same and similarly that conductivity could be used to find out the concentration of defects in ionic materials.

In the case of interstitial impurities we have an elastic relaxation is one and another is internal friction I will talk about all these things each one of them.



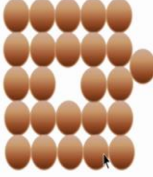
(Refer Slide Time: 33:13)

### Thermal expansion / XRD measurement


When an atom is removed from the lattice site and added to the surface, there is an increase in the number of lattice site and is reflected as expansion of the sample. Atoms adjacent to the vacant lattice site move from their normal position inwards and this causes an elastic strain. This volume strain can be measured by XRD and volume change by thermal expansion. The total volume change is

$$\frac{n}{N} = \frac{\Delta V}{V} + \left(\frac{\Delta V}{V}\right)_e$$

**N / n – total sites / total vacancies**



The diagram shows a 4x4 grid of 16 brown spheres representing atoms in a crystal lattice. The rightmost column is missing its top two spheres, creating a vacancy. The spheres in the adjacent columns are slightly shifted inward to fill the gap, illustrating the elastic strain.



NPTEL

But first let us take the simplest and the one which use precise information about the vacancy formation energy, what is it which you have to do it? This is using thermal expansion and XRD measurement suppose we take a sample and heats it, what happens then? The sample will expand that is if a sample is a perfect sample also which does not contain any defect. It has to expand in addition to it vacancies are produced. So, when an atom comes to a surface this also gives raised to relaxation and this also gives rise to expansion of the sample dimension. So, not only just the thermal expansion which takes place in addition to it vacancy creation also gives rise to expansion.

So, look is the thermal expansion gives this information suppose I try to this what will happen is that at any particular temperature wherever whatever be the temperature we are considering it when a vacancy is created as I had shown earlier some of the atom positions the neighboring atoms will come close together. So, there is going to be a relaxation that relaxation what it will do it will go raise to a slight reduction in the expansion parameter correct. So, what we measure as the thermal expansion is the relaxed change created due to the vacancy, correct.

So, if you wanted to get this information if you do an experiment which involves thermal expansion and another is with if toy do an x ray diffraction we can find out the small changes in lattice parameter those small changes in lattice parameters are coming due to the strains which are introduced you to these defects. So, essentially what we are trying

to find out is that that is what this expression says that if you look at the concentration of the vacancies which are going to be there that depends upon the volume change which is going to be there plus the delta V by V.


The volume change due to the elastic strains which are introduced into the lattice the thermal expansion give one value and this relaxation we can get it from XRD if these 2 data's are there then we can find out the concentration of the defect very accurately this is what that simple principle which is involved in this the experiment.

(Refer Slide Time: 36:04)

The volume strain  $(\frac{\Delta V}{V})_e$  can be measured by XRD and volume change  $(\frac{\Delta V}{V})$  by thermal expansion.

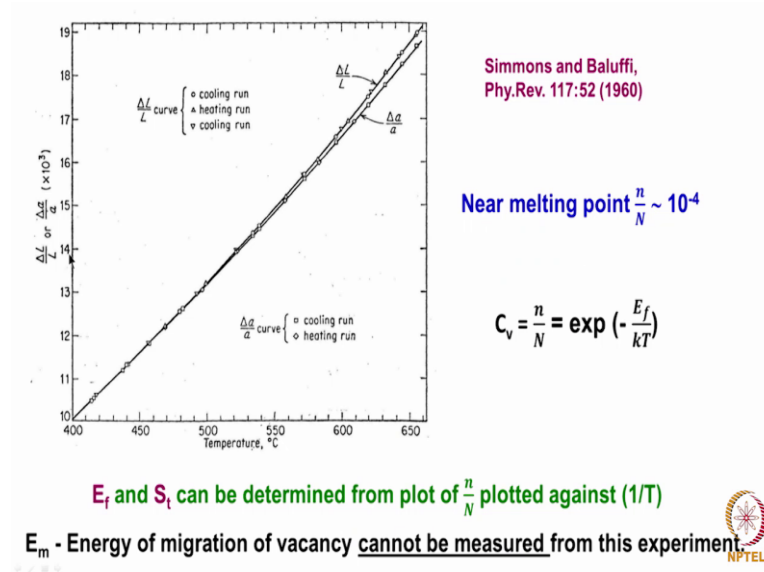
$\frac{\Delta a}{a} = \frac{1}{3} (\frac{\Delta V}{V})_e$  Lattice parameter change       $\frac{\Delta L}{L} = \frac{1}{3} (\frac{\Delta V}{V})$  Thermal expansion

$\frac{n}{N} = 3 \left( \frac{\Delta L}{L} - \frac{\Delta a}{a} \right)$       **Precise measurements are required to determine vacancy concentration**



So, these are all the terms. So, then from elasticity consideration we know that the lattice parameter change itself will be equal to look at 1 by 3 of the volume change in the strain energy term and similarly the thermal expansion delta l by l be equal to 1 by 3 of the volume change which is going to take place in thermal expansion. So, substituting all these things we can find out that by measuring this delta l by l and delta a by a we can get information about the concentration of the vacancies where that is, but what is essentially important is that precision what is the concentration of vacancies which we are looking for it is a non turned over of minus 4 adverse are much lower than that. That means, that the precision with which delta l by l has to be measured and delta a by a has to be measured is going to be very high that is what the experimental difficulty otherwise this is a very neat simple experiment with which we can get information about that defect concentration in the material.

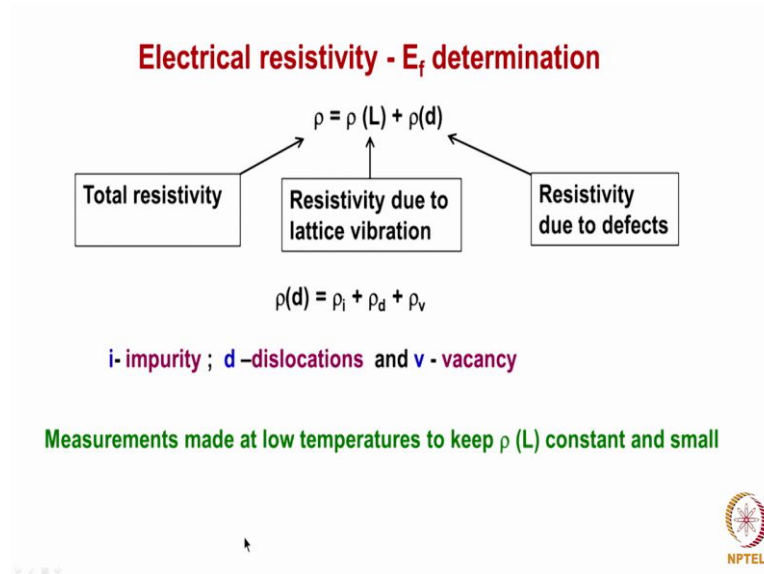
(Refer Slide Time: 37:23)



So, here what is being shown in that the plot of  $\Delta L/L$  versus temperature? It is being shown taken from the resistance Simmons and Baluffi is for here if you see it at low temperatures both of them are matching at high temperatures if you see it  $\Delta L/L$  is always shows a higher value compared to that of  $\Delta a/a$  by a correct that is because the at when a vacancies form they are going to be a relaxation which is going to take place that relaxation is essentially a contraction.

So, it shows a value which is lower whereas, suppose it is an intersection which is going to be there then it will always strain the lattice and that will add to a relaxation. So, in that case the  $\Delta L/L$  will be lower and  $\Delta a/a$  will be on the other side higher side that is what it will take place, but from this plot if you plot this one  $n/N$  versus  $1/T$ , we can get information about only the formation energy we cannot get any information about the migration energy if you have to understand about the kinetics of diffusion other diffusion characteristics we should know also that how fast that vacancy is move that information cannot be obtained from this simple experiment for which we have to do experiments which involves essentially resistivity's and another technique with which it could be done similarly that other technique the positron annihilation technique could be used to find out the vacancy concentration.

(Refer Slide Time: 39:26)



What I will; so, suppose, we consider the resistivity of a material the changes in resistivity which takes place in the material depends upon the lattice vibration that is phonon scattering the electrons, then it also occurs due to changes in the resistivity due to defects which are scattering these electrons correct. So, both of them are responsible for it.

So, essentially if you try to find out the defect itself you will try to come what all the types of defects which we can have interstitial, then we can have dislocations, then we can have impurities is also can contribute to resistivity changes, then vacancies in any material the way we can assume is that; that if we are doing experiments on a particular sample quench sample that if you have quenched it the defect concentration remains the same the type of material which he have taken the impurity concentration remains that same that will not change only change which can brought about in the resistivity is only due to the vacancy concentration variation.

That is essentially what is the assumption which is being made and; that means, that if we have to do that then the lattice contribution also is contributing to resistivity that could be quite high, if you wanted to get that information we should do this experiment at very low temperatures that if you feel, do this experiments at liquid nitrogen or liquid helium temperature then the contribution which is going to come from the lattice vibration could be reduced considerably.

And then we can easily whatever is the resistivity change which is coming and not only that if you do it at the same temperature then what we can do? It is that we measure the resistivity of that sample row at a particular temperature in an anneal condition which shows this is what the resistivity is only from the lattice vibration plus the defects which are present and if it has been a sample just been quenched it contains excess vacancy concentration if we measure at the resistivity at the same temperature this would be  $\rho$  plus  $\rho V$  because all of the defects are going to be if you find out the difference that difference will give you this difference will give you what is going to be the resistivity change which is going to take this only due to that defect which is present at that temperature.

This is a philosophy which is being used to find out the vacancy concentration, what I will do it is that about the details of this experiment and the other experiment. We will talk about it in the next class.